Evaluating dispersion in nanocomposites

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Applying a combination of techniques to characterize polypropylene nanocomposites reveals critical aspects of the data analysis and sources of misinterpretation.

The properties of plastic materials can be enhanced by incorporating additives. Nanocomposites of polymers and modified montmorillonite layered silicates (clays) already show improvement at filler contents lower than 10wt% if clay nanoparticles are homogeneously dispersed. However, achieving this dispersion and analyzing it is a highly demanding task. Although such nanocomposites have been investigated for a long time, little is available in the literature on characterizing their dispersion state. Most existing studies rely on x-ray diffraction (XRD) measurements and transmission electron microscopy (TEM). But the results of both techniques can be difficult to interpret and do not yield a useful quantitative result.

A common application of XRD, for instance, is to determine distances between interlayers on the scale of nanometers. Swelling by penetration of polymer molecules into the clay galleries (intercalation) is usually observed as an increase in the interlayer distance of the silicate platelets. When the XRD plot shows no distinct peak, the common conclusion is complete dispersion (exfoliation) of the clay in the irradiated volume. A few studies have added simple optical microscopy to the analysis of the nanocomposites because it provides an overview of the morphology and number of agglomerates on the scale of several micrometers to millimeters. But rarely are all types of analyses combined. We produced a polypropylene (PP)-clay nanocomposite and characterized the filler distribution using optical analyses, TEM, and XRD. Here, we present the results of this work.

The nanocomposite was formed into a disc by compression molding. For XRD measurements, two orthogonal pieces of the disc were cut out (see Figure 1). Additional specimens were excised and their surfaces optimized for optical microscopy to visualize agglomerates on the scale of several micrometers. The area distribution of the agglomerates in five samples was evaluated quantitatively using digital image-processing algorithms. Agglomerates smaller than 15µm were removed from the image before analysis, since they cannot be distinguished from background noise. For visualizing these and smaller particles, a TEM with an acceleration voltage of 80kV was used. Samples consisted of ultrathin cuts. Nanoscale structures were determined using XRD.

Samples were measured through both surfaces—the one parallel (P) and the other orthogonal to the surface of the disc (O)—to cover all spatial directions. All measurements were done twice at different locations on the surfaces. In addition, a second pair of samples was cut from another place on the disc, and the measurements were repeated to confirm the results. Figure 2 shows a TEM micrograph of the nanocomposites. Finely dispersed nanoparticles can be seen next to some tactoids (stacked agglomerates). This finding is typical of most polymer/clay nanocomposites produced in science and industry, which tend not to be perfectly exfoliated. Figure 3 shows micrographs of PP with 0 and 8wt% clay. As porosity and other types of defects may occur, samples with no clay were tested as well. The quantitative analysis done after processing the images yields the area size distribution shown in Figure 4.

One drawback to working with cross-sections of nanocomposites is that agglomerates end up being cut at different distances from their center, making them appear smaller than they are. A second

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disadvantage is that the value for the threshold must be set manually by the operator. Moreover, the optimum threshold depends on many imaging parameters that often are not reproducible, such as light intensity. Finally, only a very small volume of the sample can be examined. Thus, 2D techniques are good for proving the existence but not the absence of agglomerates.

3D analytical methods such as x-ray microtomography (CT) make it possible to determine the actual size and distribution of the clay agglomerates. Moreover, not only one cross-section of the sample but many hundreds can be studied at once, making the results much more reliable than those obtained using 2D methods. Figure 5 shows the CT analysis of a PP-clay nanocomposite containing 15 wt% clay. Agglomerates larger than \( \sim 10 \mu \text{m} \) can be detected, visible as light spots in the dark polymer matrix.

Figure 6 shows XRD curves of the nanocomposite that are discussed in detail elsewhere. The pattern of the curves depends strongly on the orientation of the sample during analysis. Accordingly, samples should be measured in multiple spatial directions. However, at times this can be very difficult, especially when measuring biaxially oriented nanocomposite films in the direction of extrusion (as would be the case in trying to detect agglomerates oriented parallel to the film surface).

In summary, clay particles may occur on all length scales in nanocomposites. Exfoliated structures and agglomerates can be revealed by TEM and optical microscopy, respectively. Both methods are necessary to determine which states of dispersion exist in a sample. CT

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analysis is useful in quantitatively analyzing dispersion on macroscopic length scales. Results from such 3D methods are sometimes more reliable than those from 2D methods. XRD is a 3D method that can detect agglomerated clay structures even on the scale of several nanometers. However, the results can be difficult to interpret.

In future work on characterizing nanocomposites we will also include small-angle x-ray scattering as an additional tool of investigation, in particular with respect to spatially resolved studies of large samples produced under industrial conditions.

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